Methods for Producing and Upgrading Liquid Hydrocarbons from Alberta Coal

Projects supported in part
by the Alberta/Canada
Energy Resources
Research Fund

1992
Edmonton

Alberta
ENERGY
Research and Technology Branch

92-05251/

ISBN 0-86499-890-2

Pub. No. T/267

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Foreword

Beginning in 1976, numerous projects were initiated in Alberta by industry and academic research institutions to help make better use of Alberta's energy resources.

These research, development and demonstration efforts were funded by the Alberta/Canada Energy Resources Research Fund (A/CERRF), which was established as a result of the 1974 agreement on oil prices between the federal government and the producing provinces.

Responsibility for applying and administering the fund rested with the A/CERRF Committee, made up of senior Alberta and federal government officials.

A/CERRF program priorities focused primarily on coal, energy conservation and renewable energy, and conventional energy resources. In 1988/89, a hydrogen research component was added.

Administration for the A/CERRF program was provided by staff within the Research and Technology Branch of Alberta Energy.

In recognition of the importance of coal to Alberta's economy, the Alberta Office of Coal Research and Technology was established in 1984 within Alberta Energy and Natural Resources (now Alberta Energy). Its primary purpose is to encourage the development and application of new technologies related to Alberta coals. The Office provides funding contributions to research and development projects in industry, academic institutions and other research establishments. It also monitors the progress of these projects in an overall program of improving the production, transportation and marketability of Alberta coals.

The A/CERRF program ended on March 31, 1991 and the support it provided has been replaced by funding from the Alberta government.

A series of technology transfer booklets begun in 1986 with A/CERRF support continues to make research results available to industry and others who can use the information. This service will continue until all A/CERRF projects have been described.

For more information about other publications in the series, please refer to page 21.

Methods for Producing and Upgrading Liquid Hydrocarbons from Alberta Coal

Crude oils can differ widely in their properties, making some of them more suitable than others as refinery feedstocks for particular grades of petroleum products. One way to make more efficient use of available crudes, whether they are naturally occuring or derived from bitumen or coal, is to treat them with hydrogen in a process called hydrotreating or hydroprocessing.

This procedure has the added advantage of removing certain chemical compounds containing sulphur, nitrogen and oxygen that can cause engines and furnaces to corrode. Also, petroleum products containing lower concentrations of sulphur and nitrogen compounds produce smaller quantities of sulphur oxides and nitrogen oxides when they are burned as fuels. Therefore, hydroprocessing is an important process and is expected to become increasingly important in schemes that produce synthetic crude oils from non-conventional sources of oil.

Production of synthetic crude oils by co-processing coal and heavy oil or bitumen has been the subject of research efforts in Alberta since 1979. Some of the earlier experiments were described in the publication, *Co-processing Studies of Alberta Subbituminous Coals,* while descriptions of subsequent work are found in *Methods for Producing Liquid Hydrocarbons from Alberta Coal.*

This publication describes the treatment that is necessary for these crude oils to become suitable as feedstocks for refineries. All of these research projects were funded in part by the Alberta/Canada Energy Resources Research Fund.

Hydroprocessing of Coal-Based Liquids

Although hydroprocessing has become fairly common, process improvements are needed to achieve greater efficiency and lower cost. With these objectives in mind, an investigation was undertaken from 1982 to 1985 at the University of Alberta to evaluate the performance of specific catalysts in removing undesirable chemicals during hydroprocessing, and to define better the removal mechanisms.

Initial studies concentrated on quinoline, which was selected because it is typical of nitrogen-containing compounds found in petroleum products. Furthermore, it was reasoned that any process that could efficiently remove nitrogen would also remove sulphur- and oxygen-containing compounds, because their removal is generally less difficult.

Quinoline was blended into a relatively nitrogen-free, heavy atmospheric gas oil to produce feedstocks containing different nitrogen concentrations. These blends were then added to a reactor preheated to approximately 400°C. In the reactor, the blends came in contact with hydrogen in the presence of a catalyst. Liquid reaction products were analysed for sulphur and nitrogen, while gaseous products were analysed for various low molecular weight hydrocarbons, hydrogen sulphide and hydrogen.

Seven commercial catalysts (five nickel-molybdenum types, one nickel-tungsten and one cobalt-molybdenum), plus one nickel-molybdenum catalyst modified with fluorine, were used in the laboratory-scale experiments.

Nickel-molybdenum catalysts were found to be superior to the others, primarily because they led to higher rates of nitrogen conversion. For optimal performance, the nickel-to-molybdenum ratio on the surface of the catalyst should be about 0.24. Also, it was found that catalysts, regardless of type, must undergo presulphidation treatment to produce metal sulphides. Otherwise, the hydro-desulphurization (HDS) or hydro-denitrogenation (HDN) reactions will not proceed.

After optimum reaction conditions were established for quinoline conversion, catalytic hydrodenitrogenation of a coal-based liquid (Saarbergwerke Process Oil) was investigated, using commercial catalysts. As had been found in the quinoline studies, nickel-molybdenum catalysts caused the highest rates of nitrogen conversion.

To understand better the dependence of hydrodenitrogenation on temperature, pressure, feed and product concentrations and space velocities, the kinetics of the quinoline HDN reaction were studied in detail.

By carrying out reactions under controlled conditions, which allowed individual variables to be changed, followed by analysing the reaction products, the investigators found that the experimental data could be described by two reaction rate expressions. It was observed subsequently that these mathematical relationships could not be applied directly to the hydrodenitrogenation of coal-derived liquids. However, it was concluded that the quantitative rate data for quinoline HDN can be used to screen commercial catalysts that might be used for coal liquid upgrading.

Of equal or greater importance, the investigation led to the establishment of a capability in Alberta to evaluate and develop catalysts, catalyst support substances, and promoters that could be used to provide specification-grade products from coal-derived liquids.

While this study was under way, scientists at the Alberta Research Council (ARC) and the University of Alberta carried out many coal liquefaction experiments and developed expertise in analysing the products of these reactions. Consequently, in 1987, a new round of hydroprocessing experiments was initiated at the University of Alberta, this time using liquid derived from subbituminous coal originating at the Highvale mine.

Although conventional chemical analyses of the coal-derived liquid were performed, it was believed they did not provide enough information to reveal the chemical restructuring expected to take place during hydroprocessing. Thus, a technique known as Functional Group Analysis (FGA) was used to characterize the coal-derived liquid. Practitioners of FGA view complex molecules as collections of functional groups, such as aromatic rings, alkyl groups or methyl groups, and they use various analytical techniques to quantify each type of group.

The FGA technique involves assembling various chemical analytical data in the form of linear material balance equations. These equations balance the nitrogen, sulphur, oxygen, or hydrogen content of possible functional groups - whose concentrations are unknown - against the corresponding elemental analysis for the total liquid. Information from proton-nuclear magnetic resonance, infra-red spectra, elemental analysis and specific titration procedures for nitrogen-containing structures was used to construct the set of linear equations. This study involved 20 unknown functional groups.

After the liquid was characterized by FGA, it was catalytically hydroprocessed in one step. Four catalysts were tried, and experiments were conducted to determine the effects of catalyst and temperature on the reaction chemistry. More than 20 reactor runs were completed.

Under the best conditions tried in this study, it was found that none of the one-step catalytic conversions was completed adequately because many competing reactions were occurring simultaneously. Nonetheless, substantial removal of sulphur, nitrogen and oxygen occurred. This was accompanied by complicated chemical restructuring. It was concluded that the Ni-Mo/Al_2O_3 catalyst showed the greatest promise for future investigations.

The Functional Group Analysis showed that hydroprocessing caused polycyclic groups in the coal-derived liquid to cleave, forming hydroaromatic groups. The technique also showed that hydrocracked fragments containing sulphur, nitrogen and oxygen were more difficult to hydrogenate further than were the original structures in which these elements were found.

Thermogravimetric analysis (TGA) was also tried as a method for hydrogenating coal-derived liquid in the presence of a catalyst. This technique allowed careful control of increases in the reactor temperature. The TGA results showed that significant reaction did not occur below 260°C, but productive hydrocracking occurred between 260°C and 380°C.

Concurrent with the hydroprocessing studies at the University of Alberta, some hydrotreating experiments were performed at the Alberta Research Council on products from the first reaction stage when Highvale subbituminous coal was co-processed with Athabasca bitumen. These products of co-processing had been prepared in a 2 kg/h continuous-flow, bench-scale reactor. The objectives of this upgrading study were to examine the options for removing sulphur and nitrogen and to quantify the amount of coal-derived carbon incorporated into the products from a conventional, catalytic hydrotreater in a secondary upgrading process.

The co-processed products were divided into three boiling point fractions: IBP-200°C, 201°-300°C and 301°-524°C. All these fractions contained substantially more sulphur and nitrogen than is allowable in refinery feedstocks.

Hydrotreating of the 201°-300°C and 301°-500°C fractions was carried out over a range of conditions using a continuous tubular reactor and either a Ni-Mo catalyst or a combination of Ni-Mo and Co-Mo on alumina. Besides the two catalyst options, other process conditions were varied as follows:

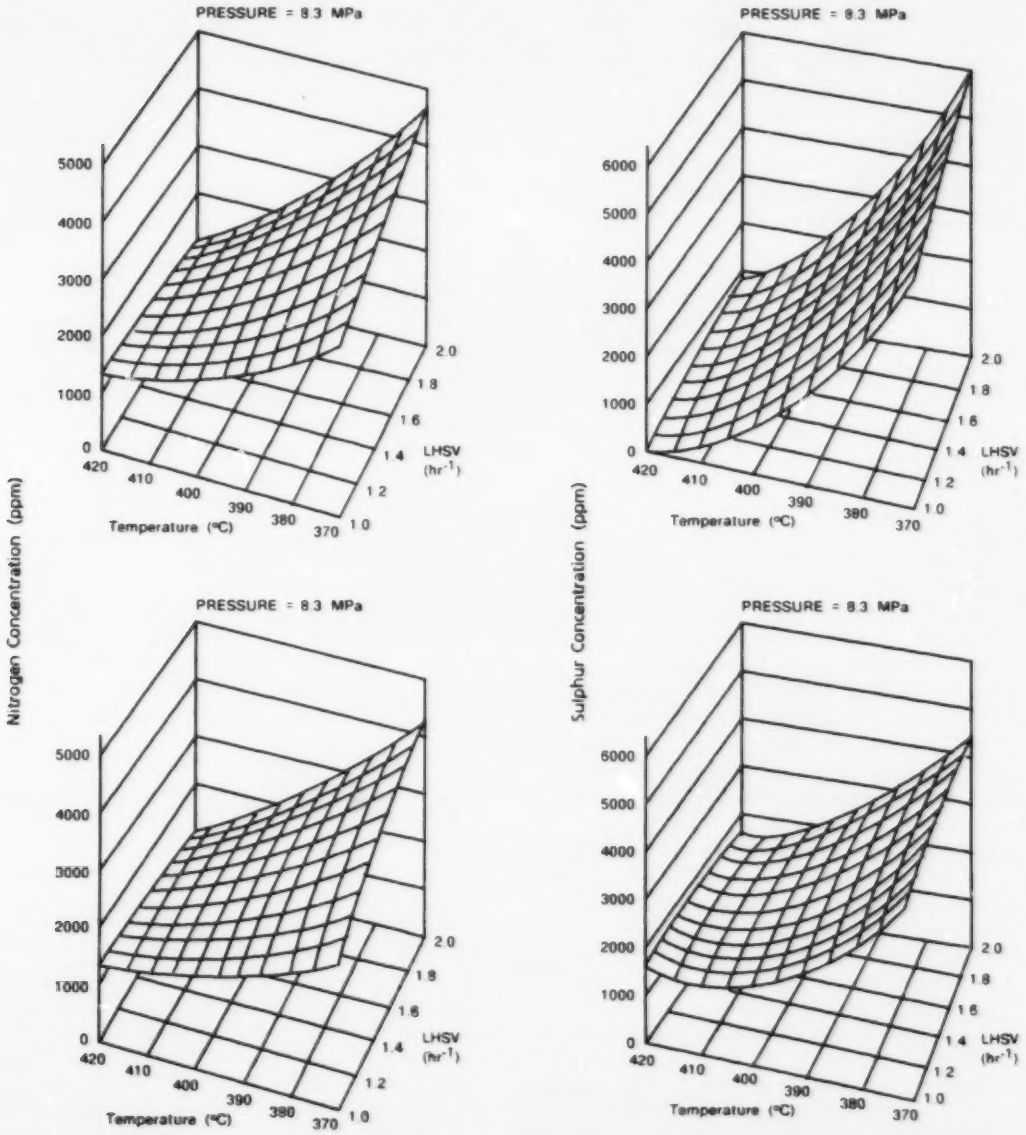
Liquid Hourly Space Velocity (LHSV), h^{-1}	1.0 - 2.0
Reaction Temperature, °C	360 - 415
Reaction Pressure, MPa	10.4 - 13.4
Hydrogen Flow Rate, vol/vol	1000/1

Analysis of the reaction products showed that all the nitrogen, or a sufficient amount of it, was removed from the upgraded products to satisfy refinery specifications, but the sulphur content of some fractions was still excessive. In decreasing order, the most effective process conditions enabling nitrogen and sulphur removal were: temperature > LHSV > pressure. It was found that a minimum process temperature of 375°C at a pressure of 13.7 MPa and LHSV of 1 h^{-1} was required to reduce heteroatom concentrations in distillates to refinery-acceptable levels.

The upgraded products were analysed to quantify the coal-derived carbon incorporated into the product fractions, using the stable isotope mass balance method. This analytical technique (described in detail later in this publication) is based on the knowledge that the $^{13}C/^{12}C$ ratio in coal is higher than in petroleum, bitumen and heavy oil, and the ratio can be expected to achieve intermediate values in synthetic crude oils. Therefore, the carbon contributed by coal to co-processed products can be calculated quantitatively from a mass balance using isotopic measurements. Similarly, the technique can be used on co-processed products that have been upgraded.

From the stable isotope mass balance analyses, it was observed that coal-derived carbon was found mainly in lighter fractions of the upgraded products. From 14.7 to 18 per cent of the Highvale coal carbon was found in distillable, upgraded products. The light oil fraction contained the most, with 9.6 per cent of the coal carbon.

Hydrotreatment of 301°C - 524°C Fraction of CED Product: Change of Nitrogen and Sulphur Concentrations with Operating Conditions



(Source: Secondary Upgrading of the First Stage Coprocessed Product, Ohuchi, T., J. Wilson and A. Chambers, Alberta Research Council, 1988.)

The hydrotreating process was then used to upgrade certain fractions of a product provided by Canadian Energy Developments Inc. (CED). This Edmonton firm is one of a group of companies that aims to design, build and operate a commercial-scale co-processing upgrader in Alberta in the 1990s. The company has simultaneously developed two co-processing schemes using either a 2 kg/h bench-scale reactor or a 227 kg (1/4 ton) per day continuous process demonstration unit, and is currently developing processes that use a counterflow reactor.

The CED product used in this study was prepared by co-processing subbituminous coal from the Vesta mine with a heavy oil known as Cold Lake vacuum bottoms. Only the 201°-524°C fraction was hydrotreated, using reactor temperatures of 360°, 375° and 390°C, and a Ni-Mo catalyst. At all three reactor temperatures, it was found that nitrogen concentrations in light oil and heavy gas oil fractions were reduced sufficently to satisfy refinery specifications. Also, nitrogen removal improved as the temperature was raised. However, a hydrotreating temperature of at least 390°C was necessary to obtain adequate nitrogen removal from the naphtha fraction. Although desired sulphur concentrations in the light oil and heavy gas oil fractions were obtained (at process temperatures exceeding 390°C), concentrations of this heteroatom were excessive in the naphtha fraction.

Consequently, a suite of statistically designed experiments was initiated to attempt improved removal of sulphur from the CED product and to develop a better understanding of the effects that process conditions have on product characteristics. As a result, sets of conditions were found that were capable of producing refinery-acceptable feedstocks. For example, requirements could be met using a reaction temperature of 415°C, a pressure of 11.0 MPa and a LHSV of 2.0 h^{-1}. The experiments also showed that temperature had the greatest effect on nitrogen and sulphur removal.

While these experiments showed that some co-processing products could be upgraded to satisfy specifications for refinery feedstocks, a second project was initiated in 1988/89 to achieve optimum removal of heteroatoms at the lowest possible conditions of reaction severity.

Tests were conducted on two slurries obtained from CED. They were the products of single-stage co-processing in a pilot plant, using Vesta coal and Cold Lake vacuum bottoms as feedstocks. Secondary upgrading was carried out in a trickle bed reactor, 96.5 cm in length and 2.54 cm in diameter. Hydrotreating experiments were conducted in the presence of a commercial Ni-Mo/Al_2O_3 catalyst mixed with an equal amount of silicon carbide. Initial experiments were carried out to attempt production of transportation fuels. For example, hydrotreated gas oil and naphtha fractions were subsequently hydrocracked or reformed by using other catalysts to produce diesel fuel or gasoline, and the light oil fraction was hydrotreated directly in an attempt to produce a diesel fuel.

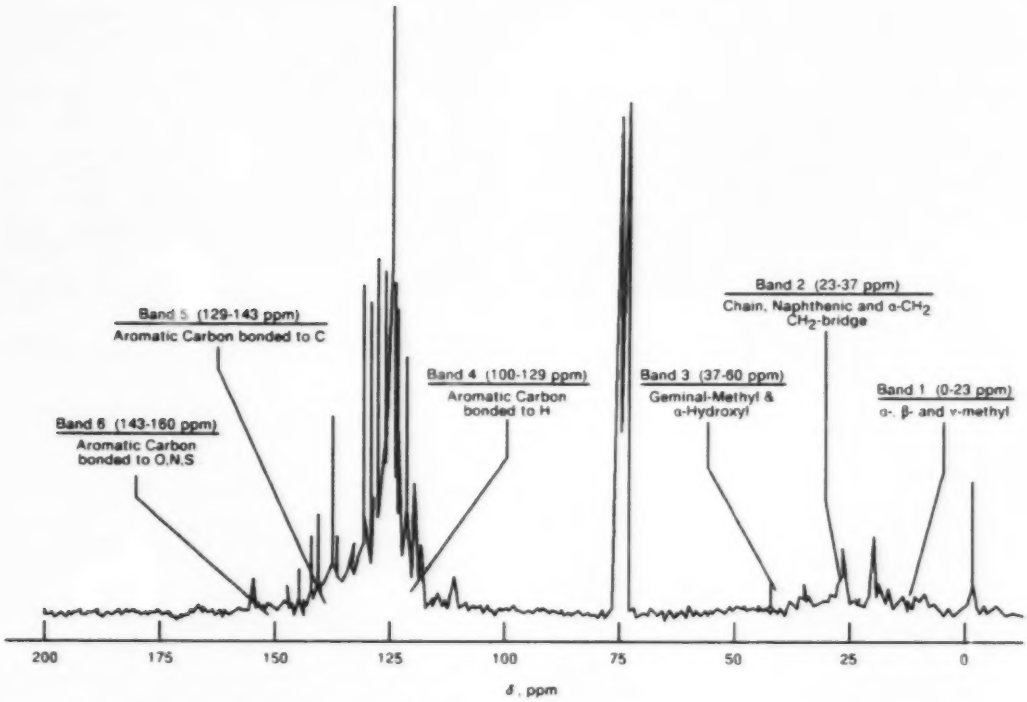
The naphtha fraction (boiling range below 177°C) of the CED slurries was hydrotreated at temperatures between 390° and 420°C, presssures of 8.3 to 12.4 MPa and weight hourly space velocity (WHSV) of 1 to 3 h^{-1}.

The light oil (boiling range from 178° to 343°C) and gas oil (boiling range above 344°C) fractions were hydrotreated at 400° to 440°C, 6.9 to 11.0 MPa and WHSV equal to 1.0 to 4.0 h^{-1}.

Using Shell Canada Limited specifications for refinery feedstocks as the reference, it was concluded that the light oil and gas oil fractions could be hydrotreated to satisfy refinery feedstock requirements for sulphur and nitrogen content, but the sulphur specifications could not be met for the naphtha fraction.

Direct hydrotreating of CED distillate produced a diesel fuel that satisfied several of the Canadian General Standards Board requirements for this type of fuel.

Band assignments for ^{13}C-NMR spectra of liquids from Highvale coal.



(Source: Functional Group Analysis of Coal Liquids, Gray, M.R. and I.G. Dalla Lana, University of Alberta, 1987.)

Functional Group Analysis

Although the composition of liquids derived from coal is so complex that it is not possible to identify and quantify every chemical compound, it is important to be able to understand the mechanisms involved in coal liquefaction or coal/bitumen co-processing. Therefore, it is necessary to characterize the major reactants and products in some manner.

In this project, initiated in 1986 at the University of Alberta, it was proposed that an approach known as Functional Group Analysis (FGA) be used. It would bridge the gap between analytical techniques capable of dissecting molecules atom-by-atom and physical chemistry measurements that provide a broad indication of certain properties.

In the first stage of this work, complex coal liquids were characterized by their various functional groups. This was done from proton nuclear magnetic resonance (NMR) spectra, carbon-13 NMR, infra-red spectra, nitrogen titration analysis and elemental analyses. The proton and carbon-13 NMR data were divided into individual bands corresponding to known chemical functionalities, and the concentrations of these functional groups were determined mathematically using computer software developed especially for this project.

With this as a background, several coal liquefaction processes were investigated in detail in co-operation with staff of the Alberta Research Council. This work incorporated some of the chemical and physical characterization methods developed at ARC.

The FGA technique was used to relate the quality of liquefaction solvents to improvements in the quality of coal liquefaction products. Thus, major liquefaction mechanisms such as dissolution of coal components in the solvent, cracking and ring-opening reactions and selective dissolution of heteroaromatic species could be followed. When Highvale coal was hydropyrolysed, for example, FGA allowed researchers to follow the step-wise transformation of reactants to products. It was observed that the paraffinic and naphthenic products obtained at low severity conditions were cracked and dehydrogenated in the gas phase to yield benzene and methane. Also, FGA was used to follow the production of tars and their subsequent conversion to other products.

During coal/bitumen co-processing, it was possible to observe hydroaromatic and naphthenic structures, originating with bitumen, being converted to aromatic compounds. It was also observed that the presence of coal caused a hydrogen deficiency that led to the formation of olefins. These are important observations in terms of producing desirable petrochemical feedstocks.

It was concluded that FGA is a valuable analytical concept and should become an integral part of all co-processing studies. It is equally applicable to bitumen or heavy oil upgrading.

Isotopic Studies of Co-processing Schemes

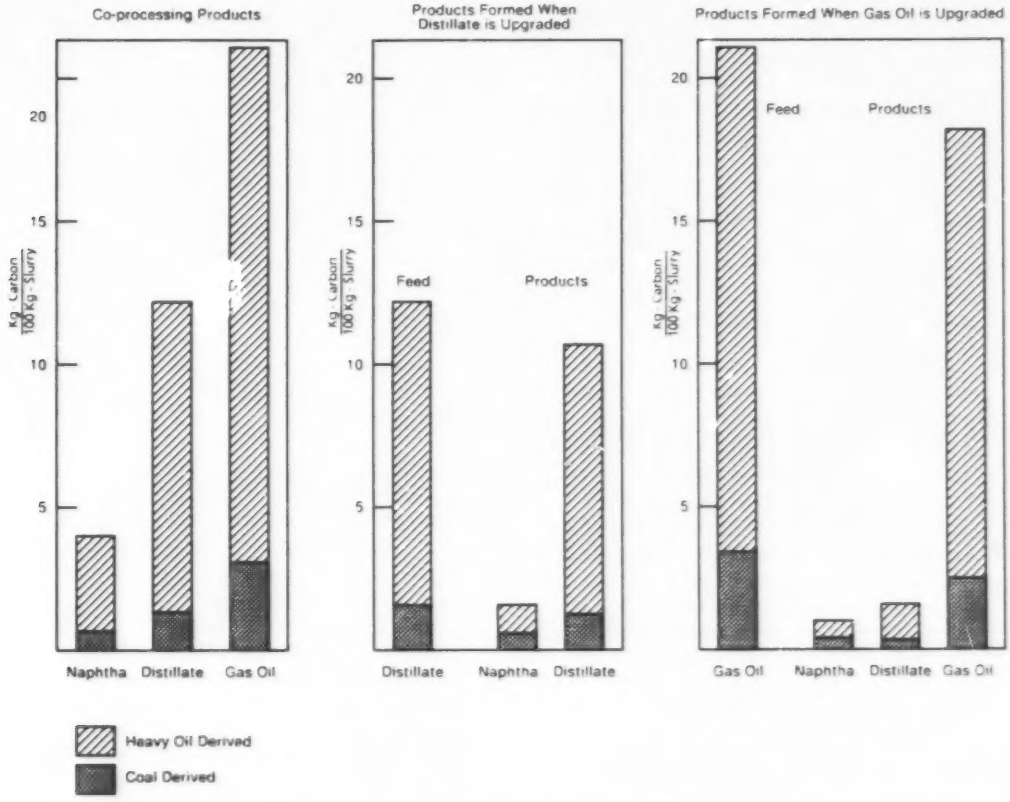
The mixture of products resulting from co-processing, and the economics of the process, are influenced by the proportions of coal and bitumen used in the feedstock. Therefore, knowing how much each feedstock component contributes to the chemical composition of the products is important, and could be the basis for a useful process control method.

It is known that the ratio of carbon-13 to carbon-12 isotopes in coal is higher than in most types of petroleum and bitumen. Thus, measurements of this ratio allow researchers to differentiate between the carbon derived from coal and that derived from bitumen in the products of coal/bitumen co-processing.

This was the basis of a research project carried out at the University of Alberta. Initially, the sensitivity of an analytical technique called isotope mass balance was determined by converting coal, bitumen and the products of co-processing experiments to carbon dioxide, and then measuring the $^{13}C/^{12}C$ ratio. It was found that the ratios for coal and bitumen differ by approximately four parts per thousand, and the ratios of co-processed products were between the values of the two feed materials.

After the accuracy and reproducibility of the technique were established, it was used to analyse the products of some co-processing experiments conducted at the Alberta Research Council. Depending on co-processing conditions, it was found that 14 to 23 per cent of the carbon in the resulting synthetic crude oil originated with coal. Of equal importance, the investigation showed that the isotope mass balance technique can be used to detect changes in the product mix and composition as the result of changes made to reaction conditions.

Distribution of Coal - Derived Carbon by Isotopic Mass Balance Analysis



(Source: Isotopic Studies on Coal/Bitumen Co-processing, Muehlenbachs, K., University of Alberta, 1990.)

Hence, the initial project was followed by a co-operative effort involving researchers at the University of Alberta and the Alberta Research Council. They used the isotope mass balance technique to determine optimum coal/bitumen reaction conditions. Also, the technique was used to evaluate the results of secondary upgrading schemes aimed at converting co-processing products into synthetic crude oils suitable as feedstocks for conventional refineries. In addition, the technique was extended to monitor the fate of nitrogen and oxygen during co-processing.

Coal solubilization in a continuous reactor was successfully monitored, and experiments conducted at 445°C in the presence of iron oxide catalyst were also monitored to gain an understanding of the factors contributing to coke production.

The isotope mass balance technique demonstrated that secondary upgrading increased the coal-derived carbon content of co-processing liquids from 19 per cent to 27 per cent.

Preliminary measurements of the ratio of ^{15}N to ^{14}N revealed a two or three per cent difference for Alberta coals versus bitumen. This suggests that a viable analytical technique is possible.

The study also included measurements of hydrogen isotope effects. It was found that partitioning of hydrogen isotopes did occur in co-processing products, and an investigation was begun to determine the cause.

Meanwhile, researchers began using the isotope mass balance technique fairly routinely to analyse the products of co-processing experiments.

Chemistry of Coal Liquefaction

The chemical changes that occur when coal is liquefied or bitumen is upgraded are complex and difficult to follow from an analytical perspective. However, when the two processes occur simultaneously, as they do in co-processing, understanding the chain of events that ultimately leads to products is even more difficult.

Consequently, a project was initiated in 1985 at the Alberta Research Council to gain a better understanding of the transformation processes that occur during coal/bitumen co-processing. The principal objective was to develop liquids characterization methods suitable for evaluating synthetic crude oils as potential oil refinery feedstocks, and to monitor differences in composition between feeds and products.

The work entailed developing chemical and physical characterization methods for co-processing feedstock and reaction products, and developing a method to characterize product performance. This involved an "analysis tree" comprising the following:

- separating high- and low-molecular weight components;
- separating asphaltenes and resins from oils;
- separating hydrocarbons into saturate and several aromatic fractions;
- separating asphaltenes by size and characterizing the fractions by FTIR and NMR methods;
- using thermogravimetric analysis for determining the detailed composition of middle and vacuum distillates;
- determining the octane and cetane indices of the middle distillate fractions of the reaction products.

Measuring the octane and cetane indices is especially important in evaluating synthetic crude oils as potential oil refinery feedstocks. This is done by establishing correlations with cetane number, a method of characterizing gasoline for diesel engines.

Normally, large samples are required for cetane-number engine tests. However, an NMR method was used to develop a relatively fast cetane index procedure suitable for small samples of coal liquids. This is a substitute for diesel engine tests. The method was calibrated with normal refinery feedstocks and was then applied to light- and middle-distillates from three coal/bitumen co-processing experiments. Correlations were established between the NMR data and the engine test.

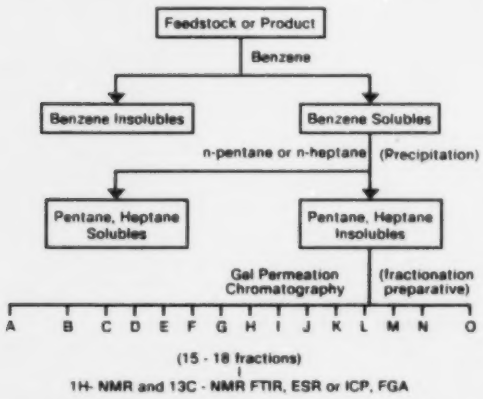
Also, a standardized procedure known as PNA analysis, for analysing paraffins, naphthenes and aromatics in naphthas, was used routinely. These methods were successfully used to analyse reaction products from a variety of liquefaction processes, including the coal/bitumen co-processing scheme of Canadian Energy Developments Inc. Special attention was paid to the asphaltene fraction because it is known to play an important role in co-processing reactions. Studies showed that the identity of the asphaltene source and

its degree of degradation to simpler molecules could be determined by these analytical methods.

The analytical procedures necessary to evaluate a synthetic crude refinery feedstock were developed successfully. This included the development and use of non-conventional analytical methods to characterize middle distillate and heavy liquid fractions.

A chemical characterization protocol involving comprehensive separation and detailed analysis of the boiling point and class fractions was developed. This characterization technique was applied to feedstock and liquid products from direct liquefaction and two coal/bitumen co-processing schemes.

Analysis Schematic for Feedstock and Product Asphaltenes


Feedstock or Product
Benzene
Benzene Insolubles
Benzene Solubles
n-pentane or n-heptane
(Precipitation)
Pentane, Heptane Solubles
Pentane, Heptane Insolubles
Gel Permeation Chromatography
(fractionation preparative)
A B C D E F G H I J K L M N O
(15 - 18 fractions)
1H- NMR and 13C - NMR FTIR, ESR or ICP, FGA

(Source: Product and Process Characterization: Analytical Evaluation of Coal/Bitumen Coprocessing Products, Selucky, M.L., Alberta Research Council, 1988.)

This approach does more than confirm the presence or absence of various classes of compounds. It allows their semi-quantitative and quantitative comparison in terms of molecular weight distribution and fate of functional groups, and it allows researchers to follow the cleavage and transformation of complex structures to simpler ones.

After this phase of the work was completed, and those properties of a synthetic crude that determine its acceptability as a refinery feedstock had been defined, the second phase of the project was begun. Its purpose was to gain a better understanding of the relationship between process chemistry and product quality.

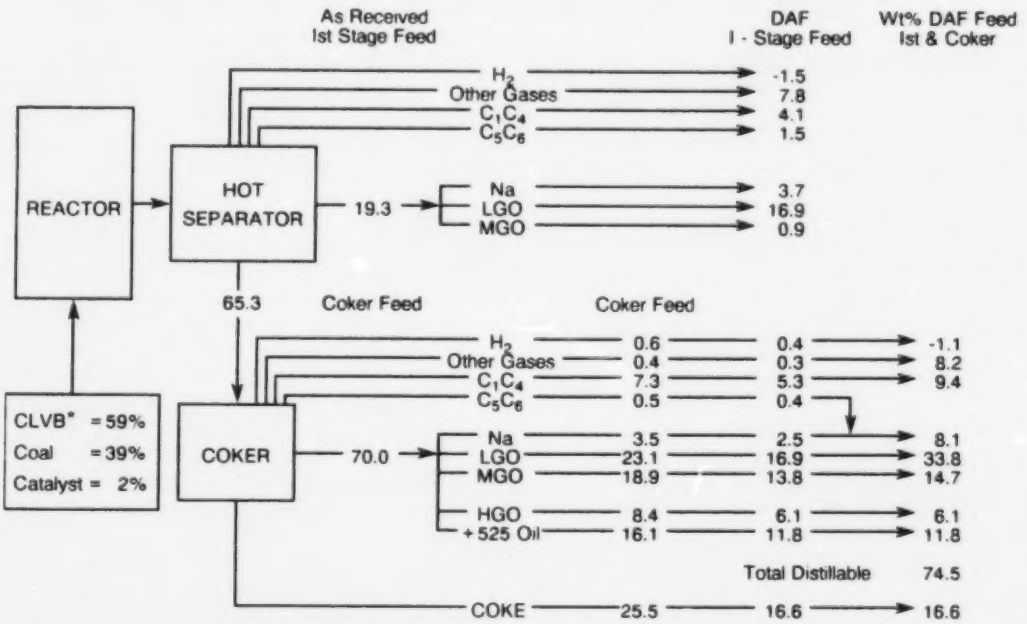
It involved three types of characterization: chemical, physical and performance. These analyses were made of the bitumen and coal feedstocks, as well as the products formed when they were co-processed. Specifically, samples of co-processed products were evaluated by nuclear magnetic resonance for cetane index, while resin samples obtained from the bench-unit experiments of Canadian Energy Developments Inc. were analyzed for resin separation and then compared. Also, samples of secondary products (middle distillate fractions) were analysed by field ionization mass spectrometry. Finally, to demonstrate the overall effectiveness of these techniques, a combination of analytical methods was used to analyse two samples of co-processing products supplied by CED.

This phase of the project was concluded with the preparation of a state-of-the-art review of analytical methods for characterizing coal liquids. Persons requiring information regarding the approximately 250-page document, titled *Coal Liquid Characterization Methods,* should contact the Alberta Research Council in Edmonton.

Co-processing Process Development

In 1986, a five-year research program funded jointly by A/CERRF and Canadian Energy Developments Inc. of Edmonton was initiated to develop processes for making synthetic crude oil from subbituminous coal and bitumen.

PYROSOL Process Product Stream



* Cold Lake Vacuum Bottoms

(Source: Canadian Energy Developments Inc.)

The objectives of the project were:

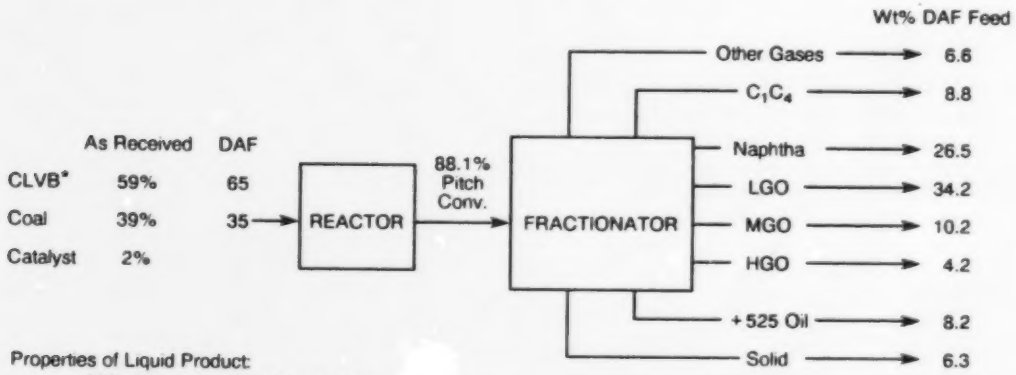
- to confirm the technical viability of co-processing as a method for producing synthetic crude oil from Alberta's subbituminous coals and bitumen;
- to develop two continuous co-processing schemes; and
- to establish appropriate upgrading technology to permit integration of process-derived liquids into refinery/product streams.

As one of a group of companies, CED proposes to design, construct and operate a commercial-scale, co-processing upgrader in Alberta in the 1990s.

One of the co-processing schemes, known as PYROSOL, is a low-severity, two-stage process. This process was initially developed in Germany, using German coals, by Gesellschaft für Kohleverflüssigung m.b.H. (GfK). It comprises mild hydrogenation and coking in a pressurized delayed coker under a hydrogen atmosphere.

The synthetic crude product from the PYROSOL process contains approximately 10 per cent naphtha, 60 per cent middle distillate and 30 per cent heavy distillate. It has the potential to be a premium product because it contains substantial quantities of middle distillate from which aviation and diesel fuels are made.

CCLC Process Product Stream



Properties of Liquid Product:

	-380	385-525	+525 Oil	C_5 + Oil
C	85.41	86.76	87.32	85.76
H	12.67	9.16	5.86	11.16
N	0.49	1.16	2.08	0.76
S	1.32	1.85	1.96	1.48
H/C	1.75	1.26	0.80	1.56

* Cold Lake Vacuum Bottoms

(Source: Canadian Energy Developments Inc.)

The second co-processing scheme, the CCLC process, involves coal solvolysis in a heavy oil slurrying medium followed by moderately severe hydrogenation of the solubilized coal and heavy oil.

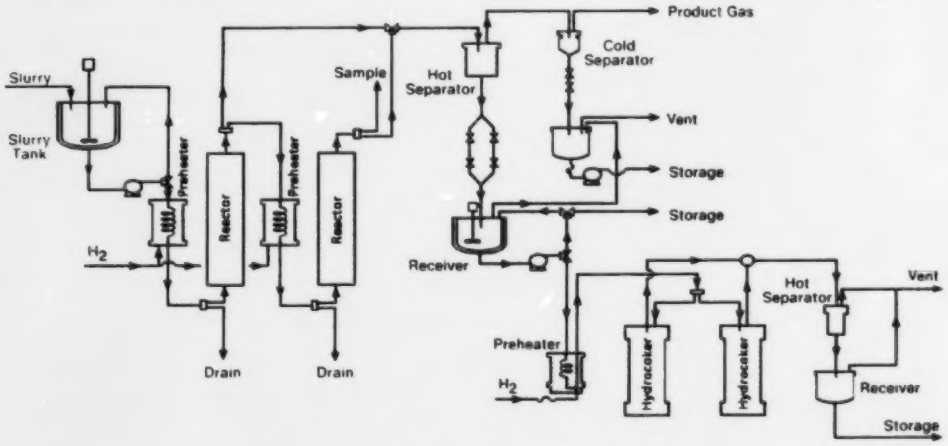
The synthetic crude from the CCLC process is a light distillate containing approximately 35 per cent naphtha, 45 per cent middle distillate and 20 per cent heavy distillate. The product is substantially lighter than that produced by the oil sands plants in Fort McMurray.

Interest in these processes, and co-processing in general, stems from the fact that use of low-cost coal lowers the feedstock cost and the overall production costs of these upgrading schemes below those used to upgrade heavy oil or bitumen alone. This not only provides a method for producing synthetic crude oil from coal, but may also be useful in upgrading heavy oil.

Since this process development project began, a 2 kg/h, two-stage hydrogenation bench-scale unit (BSU) and a 1.3 L pressurized delayed hydrocoker have been used to conduct operating-severity studies. In these studies, hydrogenation pressure, temperature and reactor residence time were varied to control the distillable oil yield and maintain a high level of pitch conversion.

Also, a 250 kg per day continuous process demonstration unit (PDU) was commissioned to allow long-duration, continuous studies to be made on a larger scale.

Process Development Unit



(Source: Canadian Energy Developments Inc.)

Later, a hydrogen recycle system (compressor and preheater) was added to the PDU to increase superficial gas velocities inside the reactors. Since the recycle system was commissioned, the PDU was operated continuously for hundreds of hours.

For both the PYROSOL and CCLC processes, a large database of process conditions and yields was established. Operating conditions have been defined to produce 70-72 weight per cent distillable oils from Cold Lake vacuum bottoms and subbituminous coal from the Vesta coalmine.

Two reactor configurations for the hydrogenation step were evaluated within the framework of a co-operative agreement between CED and GfK. All tests at CED's facilities used a co-current upflow reactor configuration, while tests of Alberta feedstocks by GfK used a counterflow reactor (CFR). These tests helped to confirm some of the advantages of CFR technology over co-current reactor designs. Development of the CFR technology will be described in a future publication.

Secondary upgrading processes were developed and defined for the treatment of co-processed products from the PYROSOL and CCLC processes. In co-operation with the Alberta Research Council, these secondary upgrading technologies were tested and a range of operating conditions was defined to allow production of desired synthetic crude oils or blending streams.

A Canadian patent, *Co-processing of Coal and Heavy Oil* was granted under application #504 954. Other patent applications in the U.S.A., Germany and Canada have been filed.

A recent estimate of the costs to build a commercial-scale co-processing plant was 25-35 per cent lower than an estimate made in 1984 in an earlier project. This reduction is the direct result of technical achievements made during the five-year period of this project. Based on these evolutionary changes in the co-processing technology, a proposal has been made to industry and governments to build a commercial-scale upgrader at the mouth of an Alberta coalmine. It would produce 28 000 barrels per day of synthetic crude oil.

Molecular Interactions Between Heavy Oil and Coal Species During Co-processing

Heavy oils used in coal/bitumen co-processing schemes are rich in asphaltenic material and reactive sulphur compounds. These oils contain three to six per cent sulphur by weight, combined in a multitude of compounds. These compounds are likely to react with the radical species produced when coal is solubilized, which could result in undesirable products. Therefore, the objective of a project carried out at The University of Calgary was to study these reactions and determine which process conditions avoid or minimize the formation of unwanted substances.

Although Alberta heavy oils contain a wide array of sulphur compounds, they can be classified in three main types: aliphatic thioethers, aromatic thioethers and condensed aromatic sulphur heterocycles.

Chemicals representing each of these classes were reacted with three chemicals having molecular structures similar to those found in coal, namely hexadecane, naphthalene and tetralin. These reactions were carried out in a small (300 ml) autoclave, under three conditions:

- thermal co-processing in the absence of hydrogen;
- thermal co-processing in the presence of hydrogen, with or without a low-activity catalyst; and
- thermal co-processing using a high-activity catalyst and a moderate pressure of hydrogen.

Also, the reactions of model compounds were repeated in the presence of a small amount of coal.

Under thermal co-processing conditions, which would be the least expensive if carried out on a commercial scale, model compounds interacted to give undesirable products. Aliphatic thioether and oxygen-containing compounds were particularly reactive and produced complex substances that were unsuitable for upgrading to refinery-acceptable feedstocks. The addition of coal to model compounds in some experiments increased the degree of reaction drastically and promoted the formation of complex materials.

When hydrogen was added, mainly desulphurised products resulted, and the formation of undesirable compounds was reduced. The addition of a high-activity alumina-supported cobalt/molybdenum catalyst facilitated the transfer of hydrogen to the model compounds. Further, it produced high rates of conversion to fully desulphurised species and eliminated undesirable reactions.

When some subbituminous coal was present, the use of alumina-supported cobalt/molybdenum catalysts produced the best yield and best quality of distillate when the mixture was heated to 425°C in the presence of hydrogen.

Combined Processing of Coal, Heavy Oil and Natural Gas

One of the major costs of coal/heavy oil co-processing is incurred in the production of gaseous hydrogen. This valuable commodity is used to suppress the formation of coke in the co-processing reactor and to upgrade the products of the co-processing reaction. Currently, hydrogen is obtained by steam reforming of natural gas, but a less-expensive source of hydrogen would significantly enhance the economics of co-processing.

In an earlier study at the University of Alberta, which was funded by A/CERRF, natural gas under high pressure was used directly as a hydrogenation agent. In the presence of tetralin and an Fe_2O_3 catalyst, natural gas (methane) caused Highvale subbituminous coal to be converted to toluene-soluble products in quantities that were equal to, or greater than, those produced when hydrogen gas was used. This suggested that substitution of methane for hydrogen would make co-processing more economically attractive if comparable product quality and yield could be achieved.

In a new project at the University of Alberta, the objective was to determine the yields and product qualities from the combined processing of coal, heavy oil and natural gas, and provide the data necessary to evaluate the feasibility of the combined processing concept.

Two types of reaction conditions were studied: coal liquefaction at 450°C using tetralin as a solvent, and co-processing of Highvale coal and Cold Lake bitumen at 410°C or 430°C. All experiments were carried out with gaseous hydrogen, nitrogen or methane at cold pressures that varied from 1 000 to 1 500 psia in the presence of Fe_2O_3 catalyst. Some experiments used ^{13}C-labelled methane to determine whether incorporation of the gas into the liquid products was significant. Reactions were carried out in a 150 mL autoclave reactor and an 8 mL microreactor.

Initial co-processing experiments, using the microreactor, produced encouraging results with methane. The product quality and yield of light products (ethane to octane) was higher when methane was used, whereas a heavy tarry material resulted when hydrogen was used. When these experiments were repeated in the larger autoclave, however, co-processing in the presence of either nitrogen or methane produced inferior results compared with the use of hydrogen. The isotope experiments showed that no detectable gas-phase methane was incorporated into the liquid products. The inconsistency between the microreactor and autoclave results was believed to have been caused by the time required to reach the desired reaction temperature. Whereas the microreactor reached 430°C in less than five minutes, it took 30 to 40 minutes for the autoclave to reach the same operating temperature. Gas pressure may have been a factor, as well.

Co-processing of Coal and Bitumen with Molten Halide Catalysts

It has been reported in the scientific literature that molten halide catalysts are excellent at cracking coal- and bitumen-related chemical structures.

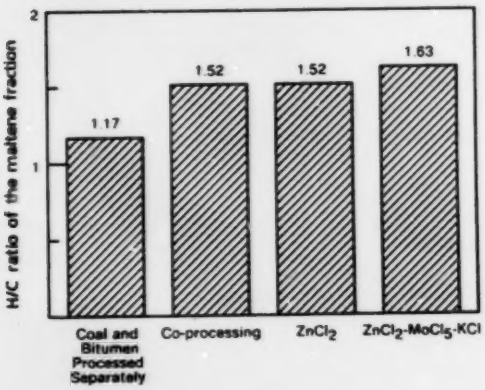
When coal is co-processed with bitumen, better solvolytic effects result. Therefore, when coal and bitumen are co-processed in the presence of a catalyst that has excellent cracking activity towards both feedstocks, better results in terms of product yield should be obtained. No work in this regard has been reported in the literature.

In this project, conducted at The University of Calgary, upgrading experiments were carried out in a batch autoclave. This was done to study the effectiveness of molten halide catalysts on the simultaneous liquefaction of a subbituminous coal and upgrading of Athabasca bitumen. Several halide catalysts were examined, including $ZnCl_2$, CuCl, KCl and $MoCl_5$. Two methods of catalyst addition to the reaction slurry were compared.

Impregnation of the coal with a catalyst-saturated methanol solution was found to be more effective than direct addition of the pulverized catalyst. The effect of different variables, such as temperature, reaction time and catalyst quantity, were studied. The optimum temperature and reaction time were found to be 400°C and two hours, respectively. Under these conditions, a net coal conversion of 75 per cent of the dry ash

free (daf) coal was achieved using a $ZnCl_2$ catalyst. The yield of maltenes was 65.75 per cent of the daf feed, while the yields of coke, asphaltene and gases were 16.42 per cent, 7.34 per cent and 10.49 per cent, respectively.

Liquid Product Quality



(Source: Coprocessing of Bitumen and Coal with Molten Halide Catalysts, Chakma, A., The University of Calgary, 1991.)

A combination of different catalysts provided even greater liquid conversion (over 80 per cent). Based on these experiments, a combination of $ZnCl_2$-KCl-$MoCl_5$ catalysts was found to be the most effective. For this catalyst combination, the liquid yield was 75.9 per cent by weight of the daf coal. Coke and gas yields were 16.75 per cent and 7.35 per cent, respectively.

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